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Review

Modeling and simulation of a direct ethanol fuel cell: An overview



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HIGHLIGHTS

- Fundamental scientific research is required to understand the complex electrochemical behavior.
- Modeling and simulation play an important role in examining the DEFC system.
- Not many work presented the fundamental issue of DEFC.
- This paper presents current progress as well as the current problem in DEFC in term of modeling and simulation.

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ABSTRACT

The commercialization of Direct Ethanol Fuel Cells (DEFCs) is still hindered because of economic and technical reasons. Fundamental scientific research is required to more completely understanding the complex electrochemical behavior and engineering technology of DEFCs. To use the DEFC system in real-world applications, fast, reliable, and cost-effective methods are needed to explore this complex phenomenon and to predict the performance of different system designs. Thus, modeling and simulation play an important role in examining the DEFC system as well as in designing an optimized DEFC system. The current DEFC literature shows that modeling studies on DEFCs are still in their early stages and are not able to describe the DEFC system as a whole. Potential DEFC applications and their current status are also presented.

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1. Introduction

Currently, the demand for power sources for applications of less than 250 W is increasing significantly in parallel with the rapid development of wireless digital communication and advanced computing technologies. Fuel cell (FC) systems with higher energy density are seen as a potential candidate to fill the growing gap between energy demand and supply for mobile applications. The FC energy density for such devices is increasing 3 to 10 times more quickly than the energy density of the lithium batteries currently in use [1]. Additionally, they offer advantages such as not requiring recharging, being more environmentally friendly and having more flexibility in system design [2,3]. For portable electronic

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applications, the size, volume, energy density and power density are more important features than efficiency. Thus, the direct alcohol fuel cell (DAFC), which is a sub category of the Proton Exchange Membrane Fuel Cell (PEMFC), has garnered much attention from researchers and manufacturers, especially for mobile and stationary applications, due to its low operating temperatures, solid state electrolyte and low efficiency compared to other types of FCs. Other DAFC advantages include easier handling and transportation, an energy-dense yet reasonably stable reaction liquid at all environmental conditions, a lack of complex steam reformers, the capability to use the traditional fuel infrastructure, and simple start up [4-7]. Foremost, the alcohol energy density is comparable to that of the current fuels, gasoline and diesel, as shown in Fig. 1. Proven to that, MTI, Toshiba, Motorola, Samsung are targeting Direct Methanol Fuel Cell (DMFC) stack for portable electrical appliances power source [8]. Instead of performance, economic viable is another important factors that contributes to better energy suppliers for portable devices. Besides, this small FC require an economically viable fuel [7,9,10] as fuel source. A few types of

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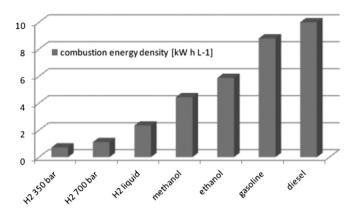


Fig. 1. Energy density comparisons of alcohols and other types of fuels [79].

substance commonly used as fuel in FC such as alcohols and hydrogen including the price were presented in Table 1. In terms of price, methanol wins over ethanol that makes it is the most widely chosen as fuel in DAFC for researches and future commercialization. However, a significant drawback of methanol such as low boiling point, inflammability, toxicity are harmful to end user if leakage during applications [4,8]. As alternative, ethanol is a potential fuel for operating FC due to fuel higher energy density, less toxicity [11– 16]. Ethanol's technical features are strong due to it is an energydense liquid so it stores compactly and it contains 35% oxygen, so it aids in clean combustion make it appealing as fuel in FC specially for portable device. Moreover, ethanol is renewable energy and it is domestically produced, via hydration of ethane and fermentation of sugars and yeasts as shown in Fig. 2. This can directly displace imported oil and petroleum products, and it provides economic support and alternative markets for agricultural crops. Previous studies have demonstrated ethanol to be a promising alternative fuel with an electrochemical activity comparable to methanol and ethanol and a crossover less severe than methanol [11–13,17–20].

However, the current Direct Ethanol Fuel Cell (DEFC) technologies are able to meet the two important features yet that is efficiency and total operation cost [21], in order to realize the DEFC commercialization. The well-known sluggish anode electro catalyst activities are at relatively low temperature (20°C-120 °C) due to problem in C–C bond breaking which lead to the low performance remains as the major technological problem [22,23]. This slow kinetics of ethanol electro-oxidation (EOR) produces unwanted intermediate products such as acetic acid and acetaldehyde. Additionally, acetic acid is a dead-end for EOR, when occurring in DEFC, as it cannot be further oxidized in the potential range typical for a working fuel cell [24]. Another major issues facing by DEFC is ethanol permeated through membrane caused mixed potential effects at cathode which lead to reduce cathode performance and fuel utilizations [25]. Besides, the DEFC system cost is still unfavorable due to expensive Pt-based catalyst and nafion based membrane [26].

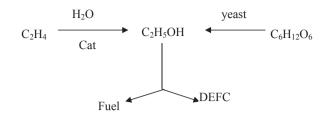


Fig. 2. Production routes of ethanol from hydration of ethane or from fermentation of sugars.

2. The applications of modeling in DEFC

Basically, the model is developed according to the specific purpose as 1) scientific understanding 2) technological development and 3) system control. As DEFC modeling still at early stages, most of the previous model was developed for scientific understanding. The scientific understanding model enables us to investigate the coupling phenomena inside DEFC towards efficiency. The DEFC efficiencies were determined from power peak density and current density. According to Heysiattalab et al. [27], these two main performance indicators are primarily influenced by design parameters such as temperature, pressure, and fuel concentration. These parameters are difficult to precisely quantify due to the complex physico-chemical processes occurring in the DEFC and involve transport processes, thermodynamics, and fluid mechanics. Fundamental scientific research is required to elucidate this complex phenomena and engineering technology. Breakthroughs in material development, the acquisition of fundamental knowledge, and the development of mathematical models and experimental tools are particularly important in current DEFC research [28].

Many experimental studies have been carried out to investigate complex phenomena in the DEFC [29–41], and a comprehensive review including DEFC developments and applications was compiled by Ref. [10]. However, experimental works have several disadvantages; for example, they are time consuming, costly, and limit the number of FC designs that could be tested. Thus, modeling and simulation are appealing as useful tools in the study of complex DEFC systems. They enable the determination of the impact of a great variety of conditions and variables on the DEFC system's global or local operating point. Furthermore, the user of the model can test various hypotheses without the risk of deterioration or destruction of the real system. Moreover, to our knowledge, no optimization work has been performed for the DEFC; and this is essential to improving the design and performance of the cell.

There are a few requirements in building a DEFC model as tabulated in Table 2. The spatial dimension which ranging from one dimensional to three dimensional as shown in Fig. 3 is important to describe FC phenomena when mass transport limitations taken into account. The higher dimensional model involved multiple complex equations that required computational solver such Computational Fluid Dynamics (CFD), Comsol Multiphysics, etc. The

Table 1
Common Fuels with properties and prices used in Direct Fuel Cells [20].

Fuels	Energy density (Wh L ⁻¹)	Standard theoretical potential, E ⁰	$-\Delta G$ (kJ mol ⁻¹)	$-\Delta H$ (kJ mol ⁻¹)	Reversible energy efficiency	Price (USD gal ⁻¹)
Methanol	4820(100%wt)	1.213	702	726	0.967	1.13
Ethanol	6280(100%wt)	1.145	1325	1367	0.969	2.04
Formic acid	1750(88%wt)	1.4	270	254.3	1.062	72.00
2-propanol	7080(100%wt)	1.122	1948	2005.6	0.971	39.1
Hydrazine	5400(100%wt)	1.615	623.4	622.2	1.002	179
Ethylene glycol	5870(100% wt)	1.220	1176.7	1189.5	0.99	37.09

Table 2Criteria in mathematical modeling

Criteria	Description		
Space dimension Temporal behavior	0D, 1D, 2D,3D Static, dynamic		
Туре	Analytical, semi-empirical, empirical		
Modeled areas Modeled phenomena domains	Stack, single cell, individual layer		
Modeled phenomena domains	Electrical (electrochemical), fluidic, thermal for single domain or multi domain		

previous DEFC modeling studies were elaborated further details according to spatial dimension in the next subtopic. Prior to that, recent DEFC modeling publications was summarized as shown in Fig. 4.

2.1. Non-dimensional models

In a non-dimensional model, the equations contain no spatial dimension. It is the simplest model presented and is only able to describe physical behavior without spatial distribution. For example, Li et al. [42], used a non-dimensional model to measure the water transport properties through an anion exchange membrane (AEM) using ethanol as fuel. The water diffusivity in AEMs demonstrates the same order of magnitude as that of Nafion membranes, and Schroeder's phenomenon also occurred in the AEM. Another non-dimensional model was developed by Ref. [43] to investigate the contribution of alloyed and non-alloyed platinum and tin in EOR with a simple model approach. In addition, the authors developed another empirical model to study the same catalyst behavior [44]. Both methods showed that the fully alloyed catalyst demonstrated better performance than the non-alloyed catalyst.

2.2. One-dimensional models

One dimensional models enable scientific understanding of the physical phenomena on a single spatial axis. The fluid, electrical and thermal domains can be modeled along the diffusion axis. Most authors that have developed a one-dimensional DEFC model created an elementary layer for each layer type (e.g., flow, diffusion, catalyst) at the anode and also at the PEM. Andreadis et al. [45] and Andreadis & Tsiakaras [46] developed one-dimensional, isothermal DEFC mathematical models to capture the relationship between mass transport and electrochemical phenomena at the anode only. The empirical equations were used to determine the diffusion

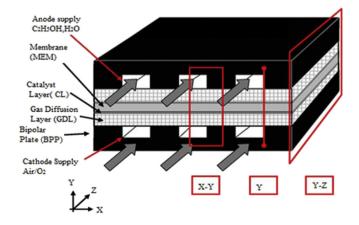


Fig. 3. Schematic illustration of spatial dimension [80].

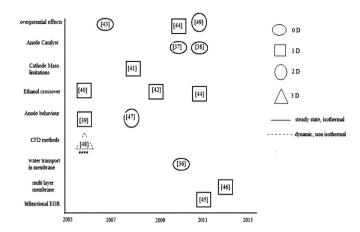


Fig. 4. Recent publications of DEFC mathematical modeling.

coefficient and mass transfer coefficient at the anode diffusion layer and anode flow channel, respectively. The rate of electrochemical reactions in the anode catalyst layer was described by a Tafel expression, and the anode over-potential was calculated along the z axis by using Ohm's law. The membrane was assumed to be fully hydrated, and hydraulic permeation effects were neglected due to equal pressure at the anode and cathode. The results showed that 10 um was the optimum catalyst layer thickness in terms of cost and performance. G. M. Andreadis et al. [47] improved the previous mathematical model by adding mass transport at the cathode and incorporating a parasitic current equation. The Tafel expression was used to determine ORR kinetics. Then, the authors developed a parametric- model based on the previous mathematical model to enhance understanding of the parameters' influence on DEFC performance [48]. According to parametric analysis, the highest power density value was obtained with an optimum ethanol feed volume of 1.0 ml.

Verma & Basu [49] developed a one-dimensional, isothermal, steady state mathematical model to investigate the electrical cell performance for multiple types of fuel, including ethanol, in a direct alkaline fuel cell. The cell performance was calculated by taking into account the concentration loss, ohmic loss and activation loss. The activation loss was derived from a multiple reaction mechanism and related rate expressions at the anode and incorporated into the Tafel expression. Ohmic losses at the membrane were calculated using empirical equations from previous studies. The concentration losses were only considered at the cathode and were described by Fick's Law, and Butler-Volmer equations were used for the rate of electrochemical reaction in the cathode catalyst laver. Pramanik & Basu [50] developed a one-dimensional, isothermal, steady state mathematical model that considered the effect of different overpotentials on DEFC performance. The activation overpotential term was formulated by considering the ethanol electro-oxidation mechanism and Butler-Volmer equation. The ohmic overpotential was modeled based on the proton conductivity of the Nafion® membrane and the ohmic losses at the electrodes, current collectors and electrode-current collector interfaces. The concentration overpotential was formulated using Fick's law, the modified Butler-Volmer equation and the process transport equations through the electrodes and electrocatalyst layers.

Another one-dimensional model was built by Suresh & Jayanti [51] to enhance the understanding of crossover phenomena. The model system was assumed to be isothermal, steady state, with a fully hydrated membrane, and linear hydraulic pressure. The Nersnt—Plank formulation and Stefan—Maxwell equation were used to describe the mass transport and multi-component

diffusion. For the membrane, the modified Schlogl approach was used to capture convection effects. Another comprehensive one-dimensional, isothermal, steady state model was produced by Meyer et al. [52]. The advantage of this model was the consideration of an EOR bifunctional reaction mechanism to determine the anode activation potential. Bahrami & Faghri [53] developed a one-dimensional, isothermal, steady state, mathematical model to examine ethanol transport through the AEM-DEFC membrane. The Tafel expression was used for both ORR and EOR. Because a single-layer AEM model was not able to physically predict ethanol transport through the membrane, the authors improved the model by applying multiple layers to properly account for the physics of ethanol diffusion and electro-osmotic effects.

2.3. Two-dimensional models

A two-dimensional mechanistic model was developed by Sousa et al. [54] to investigate component concentrations on the electrode surface. The isothermal and steady state models were compared for multiple reactions steps (partial oxidation) and a single reaction step (total oxidation) for EOR at the anode. The realistic model, which was derived from multiple rate constant values, gave component concentration profile values that were closer to the experiment values than the ideal model. Heysiattalab [55] developed a pseudo two-dimensional, steady state, isothermal model to investigate DEFC performance.

2.4. Three-dimensional models

The only three-dimensional, dynamic, non-isothermal model was developed by Sarris et al. [56] to examine the DEFC anode flow bed using computational fluid dynamics (CFD) methods. The results showed that CFD models are capable of performing a variety of flow analyses with various Reynolds numbers. The model results were in agreement with the experimental results.

3. Mass transport factors

To generate electricity, a DEFC must be supplied continuously with ethanol and oxidant. Simultaneously, the water and heat must be continuously removed to avoid strangling the cell. Ethanol and water transport through the PEM are driven by electro-osmosis, diffusion and hydraulic permeation as shown in Fig. 5. Losses due to mass transport are known as "concentration losses," which are

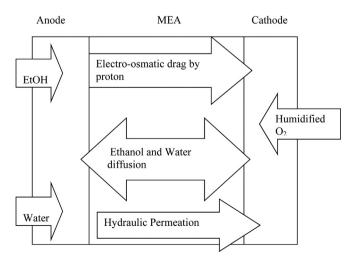


Fig. 5. Ethanol and water transport phenomena.

affected by the design of the MEAs and flow fields as well as the FC operating conditions [57]. The following characteristics are desirable: (i) membranes with low fuel permeability, (ii) anodes with improved catalysts, (iii) an anode structure that enhances twophase mass transport and catalyst utilization, (iv) selective cathode catalysts that are insensitive to fuel crossover, and (v) cathode catalyst layer structures that are less susceptible to water flooding due to the reaction and crossover from the anode [58]. Wang et al. [59] developed a new Pd/Ni foam electrode in place of the conventional carbon supported electrode, which resulted in higher surface areas in the catalyst layer, lower mass transport resistance, and improved DEFC performance. Panuwat et al. [60] revealed that the MEA without an anode MPL produced lower ethanol concentration losses than the MEA with an anode MPL. A considerable amount of work had been done to improve the catalytic activity in the EOR by introducing bimetallic catalysts [61–67] and trimetallic catalysts [41], [68–70]. Beyhan et al. [32] showed that PtSnNi/C and PtSnCo/C catalysts can achieve catalytic activity four times higher than a PtSn/C bimetallic catalyst and six times higher than a Pt/C catalyst at 80 °C.

4. Ethanol crossover

Ethanol crossover remains the main issue that impedes the widespread use and application of DEFCs. Ethanol is well known for having a lower crossover rate and affecting cathode performance less severely than methanol because of its lower permeability through the Naflon membrane and its slower electrochemical oxidation kinetics on the Pt/C cathode [71]. Thus, scientific understanding of the ethanol crossover phenomena is urgently required in order to optimize the DEFC. A mathematical model developed by Refs. [45-47] was able to describe ethanol behavior and its influencing factors in the DEFC. The model showed that the crossover rate increased linearly with the inlet ethanol concentration up to the maximum value of 10.0 M. The parasitic current formation at the cathode depended on the ethanol crossover and was greater at low current density. Another factor was that increasing the porosity of the diffusion and catalyst layers also increased the ethanol crossover rate as well as parasitic formation. This was in agreement with Kontou et al. [72], whose experiments resulted in the same findings for the ethanol permeation rate at various ethanol concentrations using a Nafion 115-based MEA. Wan and Chen [73] employed a Pt-Sn anode composite to suppress the ethanol crossover effects; however, it only enhanced the DEFC performance without reducing the ethanol crossover. Suresh & Jayanti [51] used a mathematical model to examine the effect of operating current density on ethanol crossover for various ethanol feed concentrations, as shown in Fig. 6. Bahrami & Faghri [53] used a multilayer membrane model instead of a single layer for an AEM-DEFC to properly quantify ethanol transport phenomena across the AEM and found that ethanol crossover was significantly lower in an AEM compared to a PEM.

5. Current status and future trends of the DEFC

Recently, DAFCs have gained attention for their potential application in electric vehicles, stationary electronics, and as portable power sources [33]. However, due to their low efficiency in the total conversion of carbon dioxide in DEFCs with PEM membranes, a crucial factor for large-scale applications such as in automobiles, the use of DEFCs is more practical in portable applications [67]. This is in agreement with Santasalo-Aarnio et al. [74] whose findings for power peak density for different alcohols at different configurations of MEA are shown in Fig. 7. As seen in Fig. 7, most of the peak power densities were obtained at very low

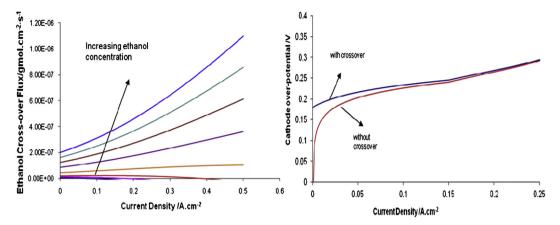


Fig. 6. Mathematical model result in describe Ethanol behavior [51].

voltages (0.1–0.3 V), which demonstrate practicality for portable applications.

However, there are number of issues need to be resolved before DEFCs are ready to enter the user market. These shortcomings are either related to DEFC technical system development or to economical issues. The problems facing DEFC system development are (1) sluggish ethanol reaction kinetics at low temperatures [75]; (2) fuel crossover, which leads to parasitic current formation and catalyst poisoning at the cathode [17]; and (3) cathode flooding, which impedes oxygen transport [76]. From an economical point of view, material costs are high, which is mainly attributed to the cost of platinum-based catalysts [77].

Instead of PEM-DEFCs and AEM-DEFCs, which have been widely investigated, a new type of DEFC known as an alkaline acid direct ethanol fuel cell (AA-DEFC) was proposed, which demonstrated the best performance among all types of DEFCs (a peak power density of approximately 360 mW cm⁻² at 60 °C) [78]. However, the PEM-DEFC exhibited lower performance compared to the AEM-DEFC using either a Pt-containing or Pt-free based catalyst [26].

In addition to material development, fluidic and thermal design components should be emphasized during commercialization of the DEFC. The DEFC design must not only include the elementary but also investigate the DEFC as a whole, including the stack and balance of the plant. Thus, a multiphase, multi-dimension, dynamic mathematical model is urgently required to capture the complex physiochemical behavior of real DEFC systems. Also, the total cost, optimum parameters, and optimization of the DEFC are necessary for successful DEFC applications.

6. Conclusion

A review of the DEFC including previous mathematical models, mass transport factors and potential applications are presented here. The modeling and simulation of the DEFC system are emphasized in this paper to provide a broad view of DEFC model pathways. To advance DEFC commercialization, better designs, materials and optimization of FCs are required. However, current DEFC models lack a few important components, and as a result, fail to imitate and predict real DEFC behavior. Further considerations,

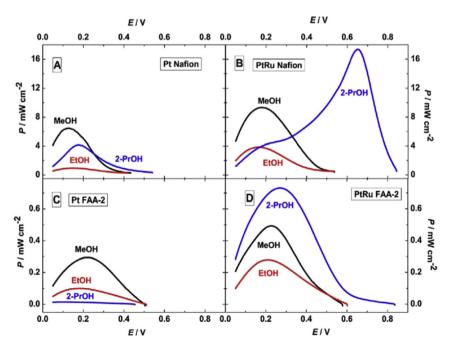


Fig. 7. The peak power densities for various fuel at different MEA configurations [74].

such as multiphase flow, gas management, fuel management, water management, and flow field design, need to be examined in order to develop a better DEFC model that is able to predict real DEFC behavior.

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References

- [1] F. Telecom and M.E. Systems, Hydrogen-fed Miniature Fuel Cell for Portable Applications.
- C.K. Dyer, J. Power Sources 106 (1-2) (Apr. 2002) 31-34.
- [3] R. Rashidi, I. Dincer, G.F. Naterer, P. Berg, J. Power Sources 187 (2) (Feb. 2009) 509-516.
- [4] Â. Lerhun, F. Delime, C. Lamy, A. Lima, C. Coutanceau, J. Le, J. Power Sources 105 (2) (2002) 283-296.
- [5] H.B. Hassan, Open. Electrochem. J. 1 (1) (Aug. 2009) 19–27.
- [6] D.M. Mackie, S. Liu, M. Benyamin, R. Ganguli, J.J. Sumner, J. Power Sources (2013) 34-41.
- [7] E. Gauthier, J.B. Benziger, Electrochim. Acta (Oct. 2013).
- [8] Z. Yuan, Y. Zhang, W. Fu, Z. Li, X. Liu, Energy 51 (Mar. 2013) 462-467.
- [9] Z.-Y. Deng, J.M.F. Ferreira, Y. Sakka, J. Am. Ceram. Soc. 91 (12) (2008) 3825-
- [10] M.Z.F. Kamarudin, S.K. Kamarudin, M.S. Masdar, W.R.W. Daud, Int. J. Hydrogen Energy (Sep. 2012) 1–16.
- [11] Y. Guo, Y. Zheng, M. Huang, Electrochim. Acta 53 (7) (Feb. 2008) 3102–3108.
- S. Song, P. Tsiakaras, Appl. Catal. B Environ. 63 (3-4) (Mar. 2006) 187-193.
- [13] N. Wongyao, a. Therdthianwong, S. Therdthianwong, Energy Convers. Manag. 52 (7) (Jul. 2011) 2676-2681.
- [14] G. García, N. Tsiouvaras, E. Pastor, M.A. Peña, J.L.G. Fierro, M.V. Martínez-Huerta, Int. J. Hydrogen Energy 37 (8) (Apr. 2012) 7131-7140.
- [15] P. Ekdharmasuit, A. Therdthianwong, S. Therdthianwong, Fuel (2013) 69-76.
- [16] N.A.M. Barakat, M.A. Abdelkareem, H.Y. Kim, Appl. Catal. A Gen. (2013) 193-198
- [17] T. Lopes, E. Antolini, E. Gonzalez, Int. J. Hydrogen Energy 33 (20) (Oct. 2008) 5563-5570.
- [18] T. Lopes, E. Antolini, F. Colmati, E.R. Gonzalez, J. Power Sources 164 (1) (Jan. 2007) 111-114.
- [19] L.C. Battirola, J.F. Schneider, Í.C.L. Torriani, G. Tremiliosi-Filho, U.P. Rodrigues-Filho, Int. J. Hydrogen Energy 38 (27) (Sep. 2013) 12060-12068.
- [20] J. Bentley, R. Derby, Ethanol & Fuel Cells: Converging Paths of Opportunity, 2001.
- [21] Y. Ma, G.G. Karady, A. Winston, P. Gilbert, R. Hess, D. Pelley, Energy Convers. Manag. 50 (2) (Feb. 2009) 422-430.
- [22] H. Yu, D. Zhou, H. Zhu, J. Solid State Electrochem. 18 (1) (2014) 125-131.
- [23] C. Lamy, T. Jaubert, S. Baranton, C. Coutanceau, J. Power Sources 245 (Jan. 2014) 927-936.
- [24] A. Jablonski, A. Lewera, Appl. Catal. B Environ. 115–116 (Apr. 2012) 25–30.
- [25] M.S. Naughton, C.E. Tornow, Y. Bonita, H.-R. "Molly" Jhong, F.R. Brushett, A.A. Gewirth, P.J.A. Kenis, Int. J. Hydrogen Energy 38 (21) (2013) 8980–8991.
- [26] a. Brouzgou, a. Podias, P. Tsiakaras, J. Appl. Electrochem. 43 (2) (Dec. 2012) 119-136.
- [27] S. Heysiattalab, M. Shakeri, M. Safari, M.M. Keikha, J. Ind. Eng. Chem. 17 (4) (Jul. 2011) 727-729.
- [28] Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, Appl. Energy 88 (4) (Apr. 2011) 981-1007.
- [29] S. Song, G. Wang, W. Zhou, X. Zhao, G. Sun, Q. Xin, S. Kontou, P. Tsiakaras, The Effect of the MEA Preparation Procedure on Both Ethanol Crossover and DEFC Performance, vol. 140, 2005, pp. 103-110.
- [30] Z.-B. Wang, G.-P. Yin, Y.-G. Lin, J. Power Sources 170 (2) (Jul. 2007) 242–250.
- [31] J.J. Linares, T. a. Rocha, S. Zignani, V. a. Paganin, E.R. Gonzalez, Int. J. Hydrogen Energy 38 (1) (Jan. 2013) 620-630.
- [32] S. Beyhan, C. Coutanceau, J.-M. Léger, T.W. Napporn, F. Kadırgan, Int. J. Hydrogen Energy 38 (16) (2013) 6830-6841.
- [33] A.D.S. Gomes, J.C. Dutra Filho, Int. J. Hydrogen Energy 37 (7) (Apr. 2012) 6246-6252.
- [34] S. Rousseau, C. Coutanceau, C. Lamy, J.-M. Léger, J. Power Sources 158 (1) (2006) 18-24.
- [35] C.V. Rao, B. Viswanathan, Electrochim. Acta 55 (8) (Mar. 2010) 3002–3007.

- [36] Y.S. Li, T.S. Zhao, Z.X. Liang, Performance of Alkaline Electrolyte-Membrane-Based Direct Ethanol Fuel Cells, vol. 187, 2009, pp. 387–392.
- [37] K. Fatih, V. Neburchilov, V. Alzate, R. Neagu, H. Wang, J. Power Sources 195 (21) (Nov. 2010) 7168-7175.
- [38] M.C. Figueiredo, A. Santasalo-Aarnio, F.J. Vidal-Iglesias, J. Solla-Gullón, J.M. Feliu, K. Kontturi, T. Kallio, Appl. Catal. B Environ. (2013) 378–385.
- [39] F.L.S. Purgato, S. Pronier, P. Olivi, a. R. de Andrade, J.M. Léger, G. Tremiliosi-Filho, K.B. Kokoh, J. Power Sources 198 (Jan. 2012) 95-99.
- [40] D.D. James, P.G. Pickup, Electrochim, Acta 78 (Sep. 2012) 274–278.
- [41] J. Tayal, B. Rawat, S. Basu, Int. J. Hydrogen Energy 36 (22) (Nov. 2011) 14884-14897.
- [42] Y.S. Li, T.S. Zhao, W.W. Yang, Int. J. Hydrogen Energy 35 (11) (Jun. 2010) 5656-5665.
- [43] E. Antolini, E.R. Gonzalez, Electrochim. Acta 55 (22) (Sep. 2010) 6485-6490.
- [44] E. Antolini, Int. J. Hydrogen Energy 36 (17) (Aug. 2011) 11043–11047.
- [45] G. Andreadis, S. Song, P. Tsiakaras, J. Power Sources 157 (2) (Jul. 2006) 657-665
- [46] G. Andreadis, P. Tsiakaras, Chem. Eng. Sci. 61 (22) (Nov. 2006) 7497-7508.
- [47] G.M. Andreadis, A.K.M. Podias, P.E. Tsiakaras, J. Power Sources 181 (2) (Jul. 2008) 214-227.
- [48] G.M. Andreadis, A.K.M. Podias, P.E. Tsiakaras, J. Power Sources 194 (1) (Oct. 2009) 397-407.
- [49] a. Verma, S. Basu, J. Power Sources 168 (1) (May 2007) 200-210.
- [50] H. Pramanik, S. Basu, Chem. Eng. Process Process Intensif. 49 (7) (Jul. 2010) 635-642
- [51] N.S. Suresh, S. Jayanti, Int. J. Hydrogen Energy 36 (22) (Nov. 2011) 14648-14658
- [52] M. Meyer, J. Melke, D. Gerteisen, Electrochim. Acta 56 (11) (Apr. 2011) 4299-4307
- [53] H. Bahrami, A. Faghri, J. Power Sources 218 (Nov. 2012) 286-296.
- [54] R. Sousa, D.M. dos Anjos, G. Tremiliosi-Filho, E.R. Gonzalez, C. Coutanceau, E. Sibert, J.-M. Léger, K.B. Kokoh, J. Power Sources 180 (1) (May 2008) 283–293.
- S. Heysiattalab, Smart Grid Renew. Energy 02 (04) (2011) 427-433.
- [56] I. Sarris, P. Tsiakaras, S. Song, N. Vlachos, Solid State Ionics 177 (19-25) (Oct. 2006) 2133-2138.
- a. Heinzel, V.M. Barragán, J. Power Sources 84 (1) (Nov. 1999) 70-74.
- [58] W. Qian, D.P. Wilkinson, J. Shen, H. Wang, J. Zhang, J. Power Sources 154 (1) (Mar. 2006) 202-213.
- [59] Y.-L. Wang, Y.-Q. Zhao, C.-L. Xu, D.-D. Zhao, M.-W. Xu, Z.-X. Su, H.-L. Li, J. Power Sources 195 (19) (Oct. 2010) 6496-6499.
- [60] S. T. Panuwat Ekdharmasuit, Apichai Therdthianwong, The role of an anode microporous layer in direct ethanol fuel cells at different ethanol concentrations, in International Journal of Hydrogen Energy.
- [61] H. Li, G. Sun, L. Cao, L. Jiang, Q. Xin, Electrochim. Acta 52 (24) (Aug. 2007) 6622-6629.
- [62] C. Lamy, S. Rousseau, E. Belgsir, C. Coutanceau, J.-M. Léger, Electrochim. Acta 49 (22-23) (Sep. 2004) 3901-3908.
- [63] E. Antolini, J. Power Sources 170 (1) (Jun. 2007) 1–12.
- A.O. Neto, E. V Spinacé, Preparation of PtSn/C Electrocatalysts by an Alcohol-Reduction Process Using Different Conditions for Ethanol Electro-oxidation, 2009, p. 2013.
- Y. Wang, S. Song, G. Andreadis, H. Liu, P. Tsiakaras, J. Power Sources 196 (11) (Jun. 2011) 4980-4986.
- [66] S.C. Zignani, E.R. Gonzalez, V. Baglio, S. Siracusano, A.S. Aricò, Investigation of a Pt 3 Sn/C Electro-Catalyst in a Direct Ethanol Fuel Cell Operating at Low Temperatures for Portable Applications, vol. 7, 2012, pp. 3155–3166.
- [67] J.J. Linares, S.C. Zignani, T. a. Rocha, E.R. Gonzalez, J. Appl. Electrochem. 43 (2) Nov. 2012) 147-158.
- [68] J. Ribeiro, D.M. dos Anjos, K.B. Kokoh, C. Coutanceau, J.-M. Léger, P. Olivi, a. R. de Andrade, G. Tremiliosi-Filho, Electrochim. Acta 52 (24) (Aug. 2007) 6997-7006.
- [69] J. Barroso, A.R. Pierna, T.C. Blanco, N. Ruiz, Int. J. Hydrogen Energy (2013).
- [70] J. Goel, S. Basu, Energy Procedia 28 (Jan. 2012) 66-77.
- S. Song, W. Zhou, Z. Liang, R. Cai, G. Sun, Q. Xin, V. Stergiopoulos, P. Tsiakaras, Appl. Catal. B Environ. 55 (1) (Jan. 2005) 65-72.
- [72] S. Kontou, V. Stergiopoulos, S. Song, P. Tsiakaras, J. Power Sources 171 (1) (Sep. 2007) 1-7.
- C.-H. Wan, C.-L. Chen, Int. J. Hydrogen Energy 34 (23) (Dec. 2009) 9515–9522.
- [74] A. Santasalo-Aarnio, S. Tuomi, K. Jalkanen, K. Kontturi, T. Kallio, Electrochim. Acta 87 (Jan. 2013) 730-738.
- [75] J. Friedl, U. Stimming, Electrochim. Acta (Jan. 2013) 41-58.
- Y.S. Li, T.S. Zhao, R. Chen, J. Power Sources 196 (1) (Jan. 2011) 133-139.
- [77] M. Zhiani, H. a. Gasteiger, M. Piana, S. Catanorchi, Int. J. Hydrogen Energy 36 (8) (Apr. 2011) 5110-5116.
- [78] L. An, T.S. Zhao, Int. J. Hydrogen Energy 36 (16) (Aug. 2011) 9994-9999.
- V. Hacker, A. Hofer, M. Bodner, C. Grimmer, A. Schenk, in: 8th A3PS Conference Eco-Mobility 2013, 2013.
- [80] D. Cheddie, N. Munroe, J. Power Sources 147 (1-2) (Sep. 2005) 72-84.